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CHAPTER 23

Electron-Oxidation of Aromatic Molecules, Layer-Form Boron Nitride and Graphite

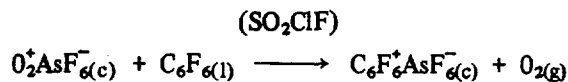
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INTRODUCTION

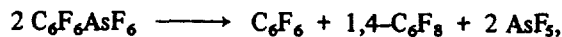
This paper reviews that work at Berkeley which, over the past eight years, has been devoted to the electron-oxidation of aromatic molecules and polycyclic, electron-delocalized systems. Graphite is the infinite-sheet relative of such molecules and its electron-oxidation has been our major interest recently. The first salt of electron-oxidized layer form boron nitride had resulted from these studies, and a greater understanding has been achieved of the factors which are important for intercalation of graphite by oxidizers. The polycyclic hydrocarbon salts and the boron nitride and graphite salts are good electrical conductors and some of the last may have value as electrode materials.

PERFLUOROAROMATICS

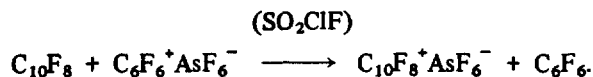
The relatively high ionization potential of hexafluorobenzene (10.0 eV) requires [1] an extraordinary oxidizer such as the dioxygenyl cation, O_2^+ :



and this reagent is also effective for the electron-oxidation of perfluorotoluene [2] and perfluoropyridine [3]. Since the salt, $\text{C}_6\text{F}_6^+\text{AsF}_6^-$, is thermodynamically unstable, and has a half-life of only an hour or so at room temperature, and yields volatile products:



it is the reagent of choice [4] for the electron-oxidation of the highest fluoroaromatics, for example:



These highly coloured salts (C_6F_6^+ , yellow; $\text{C}_{10}\text{F}_8^+$, dark green; $\text{C}_5\text{F}_5\text{N}^+$, deep blue) are simple paramagnets. This is consistent with structural evidence. The salt $\text{C}_6\text{F}_6^+\text{AsF}_6^-$ has a rhombohedral unit cell containing one formula unit ($a = 6.60(1)$ Å; $\alpha = 106.0(1)^\circ$; $V = 246.1$ Å³) in which each ion is surrounded by eight ions of the other kind, in a rhombohedral variant of the CsCl structure. The structure of $\text{C}_{10}\text{F}_8^+\text{AsF}_6^-$ is less certain, but the X-ray powder data has been indexed on the basis of a tetragonal cell ($a = 8.24(1)$; $c = 18.44(9)$; $V = 1252$ Å³, $Z = 4$) the dimensions and symmetry of which indicate a simple ionic lattice [4].

The rhombohedral, unimolecular, unit cell of $\text{C}_6\text{F}_6^+\text{AsF}_6^-$ was unexpected since a Jahn-Teller distortion was anticipated for the cation. Evidently the distortion is too subtle to be manifest at temperatures down to -130° , since single crystals remain rhombohedral down to that temperature.

Undoubtedly the synthetic approaches for the smaller perfluoroaromatics will be applicable to the synthesis of salts of the perfluoropolycyclic carbon species, but it appears that the polycyclic hydrocarbons can also be successfully electron oxidized to yield salts. The larger polycyclic cations provide for the possibility of enforced overlap of cation with cation, since the effective thickness of an anion such as AsF_6^- (see Fig. 23.1) is approximately 4.7 Å, whereas that of a polycyclic hydrocarbon or aromatic molecule is ~ 3.4 Å. It was the possibility of such overlap and the impact that such overlap could have upon the electrical conductivity of the salts, which encouraged the attempts to synthesize them.

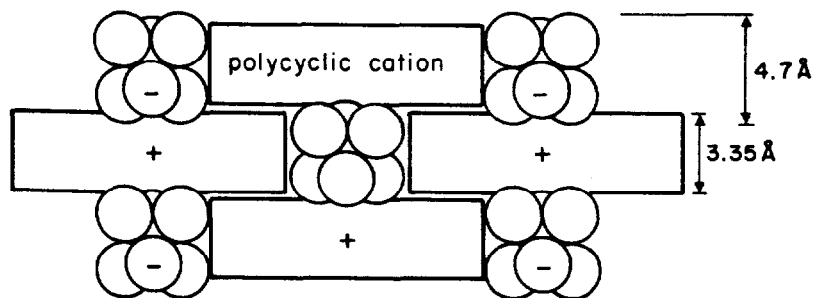
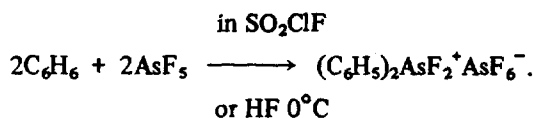


Fig. 23.1 – A possible structural model for AsF_6^- salts of polycyclic hydrocarbon cations.

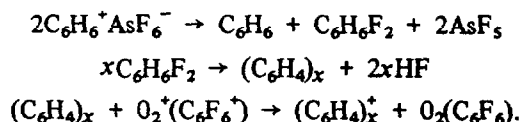
ELECTRON-OXIDATION OF POLYCYCLIC HYDROCARBONS AND BENZENE

Oxidants such as $O_2^+AsF_6^-$ or $C_6F_6^+AsF_6^-$ can be used in the oxidatively robust solvent SO_2ClF , if the temperature is kept below -20° , but it is then a poor solvent for the polycyclic hydrocarbons. Interaction of hydrocarbons such as anthracene, phenanthrene, or coronene with these oxidizers, in that solvent yields deeply coloured solids (with deep blue or purple hue). These solids are amorphous to X-rays. The packed finely divided solids conduct electricity and the conductivity appears to be at least as good as that of graphite. Unfortunately the absence of crystalline material has prevented structural work and meaningful conductivity studies.

Interaction of benzene with $O_2^+AsF_6^-$ or $C_6F_6^+AsF_6^-$ always yielded a mixture of two solids, one a colourless solid, soluble in anhydrous hydrogen fluoride, and the other a blue-black electrically conducting, insoluble solid. The former has proved [4] to be the salt $(C_6H_5)_2AsF_2^+AsF_6^-$ which can be made quantitatively by the interaction:



The latter is a salt of polyparaphenylene, $(C_6H_4)_x^+AsF_6^-$. Values of x have been observed between 1.8 to 4.4. It depends upon the relative quantities of benzene and oxidant and upon the reaction conditions. It seems that electron-oxidation of benzene is a first-step to this polymer salt and a plausible reaction sequence is:

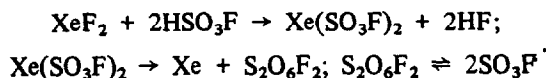


BORON NITRIDE OR GRAPHITE WITH $S_2O_6F_2$

Salts derived by electron oxidation of graphite have long been known [5] but such materials gained a new significance with the demonstration by Ubbelohde and his coworkers [6] that they were electrical conductors (in the *ab* plane) comparable with or, in some cases, superior to aluminium metal. Graphite itself is a semimetal, the conductivity being due to a small overlap of the valence band (fully occupied at 0°K) and the *conduction band* (empty at 0°K). The electron-oxidation of the graphite which occurs on formation of salts such as the first stage bisulfate, $C_{24}^+HSO_4^- \cdot 2H_2SO_4$, removes electrons from the valence band and thus increases the number of electron-hole carriers. This provides the basis

for the order of magnitude increase in conductivity which accompanies the oxidation of the graphite [7].

The fluorosulfate radical, SO_3F^\cdot , first discovered by Dudley and Cady [8] and conveniently preparable [9] in high purity by decomposition of xenon bis-fluorosulfate, $Xe(SO_3F)_2$:



offered the prospect of being able to prepare an analogue of the bisulfate, $C_{24}^+HSO_4^- \cdot 2H_2SO_4$, in which a much higher positive charge in the carbon layers could be achieved, namely: $C_{24}^{3+}3SO_3F^-$. Indeed treatment of graphite with $S_2O_6F_2$ yields fluorosulfates [10] for which the limiting composition is approximately C_7SO_3F . This is a blue solid which is vacuum stable at room temperature and, as an electrical conductor, is superior to graphite in the *ab* plane.

If graphite is partially intercalated by SO_3F and then treated with fluorosulfonic acid first-stage material of approximate composition $C_7(SO_3F)_x(HSO_3F)_{1-x}$ is formed [11]. Samples have been prepared where *x* is as small as one-third and even lower values may be attainable. Such acid-rich materials have higher *ab* plane electrical conductivities than the fully oxidized material. This is not understood. X-ray powder photography also shows that the acid containing material is always more crystalline than that devoid of acid. This indicates that $C_7(SO_3F)_x(HSO_3F)_{1-x}$ has a more ordered structure than C_7SO_3F . The higher order in the acid-rich material could be a consequence of hydrogen bonding between guest species but it may also signify that the carbon layers in the $C_7(SO_3F)_x(HSO_3F)_{1-x}$ material are more regular than in C_7SO_3F . Certainly there is a correspondence here (see below) with the instability of single crystals of the C_8MF_6 salts, such as C_8AsF_6 (which degenerate to *ab* plane-disordered slabs) whereas single crystals of C_8AsF_5 retain their crystallinity over long periods.

Each of the materials C_7SO_3F and $C_7(SO_3F)_x(HSO_3F)_{1-x}$ is metallic and they will interact when mixed to yield a material of an intermediate composition which is determined merely by the molar ratio of the reactants. The data for the *c* and *a* axis parameters given in Fig. 23.2 indicate that the *c* parameter is essentially linearly dependent upon the composition. Of course the interaction involves simply the transfer of protons and electrons between the reactants. This appears to be facile [11] even with the mixed solids, but traces of acid may be necessary.

Although layer-form boron nitride is an electrical insulator because of the more than 3 eV gap between the *valence* and *conduction* bands, the close structural relationship to graphite, illustrated in Fig. 23.3, suggested that oxidative intercalation of the nitride might be achieved by SO_3F . This proved to be so [10]. The first-stage blue salt has a composition close to $(BN)_{3.7}SO_3F$. The

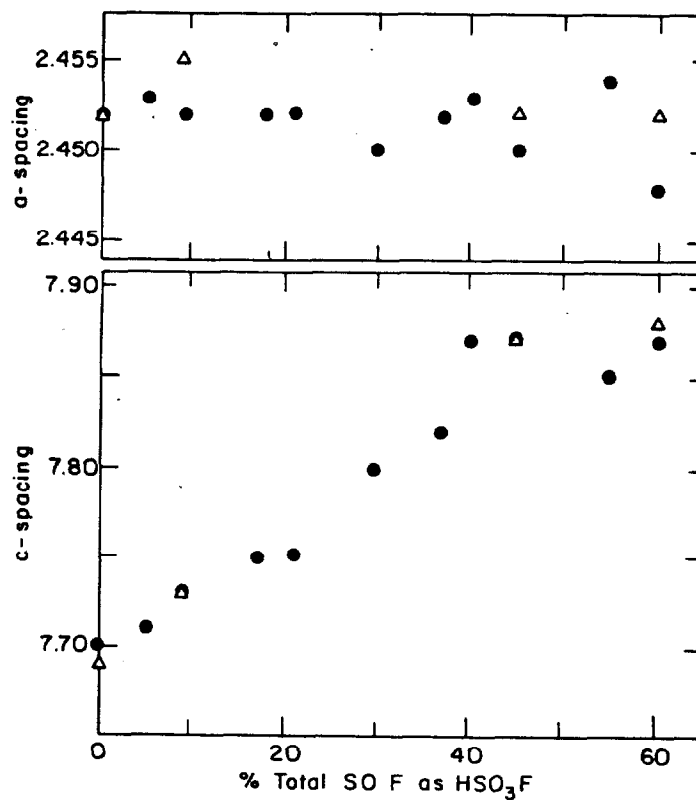


Fig. 23.2 – Lattice parameters as a function of composition for $C_7(SO_3F)_x-(HSO_3F)_{1-x}$. Triangles indicate duplicate run of a given composition.

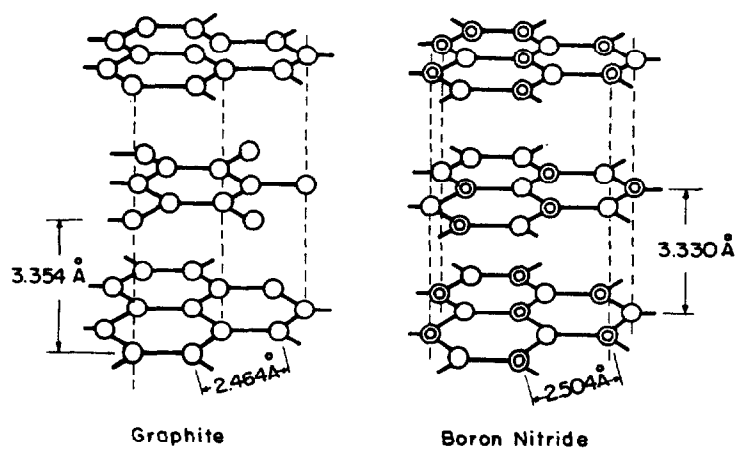


Fig. 23.3 – Comparison of the structures of graphite and layer-form boron nitride.

c axis is larger than in the graphite case (8.0(1) and 7.7(1) Å respectively). This may mean that the SO_3F^- groups are oriented with their threefold axes parallel to *c*, the negative end of the dipole being pointed at the more positive B atoms and away from the N atoms. Unfortunately the poor crystallinity of the $(\text{BN})_{3.7}\text{SO}_3\text{F}$ and its instability (it slowly generates BF_3) have frustrated structural studies. Crude electrical conductance studies show that the powdered boron nitride salt is at least comparable with graphite powder. Oxidation of boron nitride with $\text{S}_2\text{O}_6\text{F}_2$ in the presence of HSO_3F suggests that acid salts comparable with the graphite analogues can be prepared. Unfortunately the instability [12] of boron nitride with respect to hydrogen fluoride and to fluorine has limited the range of oxidizers to be applied to it.

HEXAFLUOROMETALLATES OF GRAPHITE

The steady increase in oxidizing capability with atomic number of the transition metal, in the hexafluorides of the third transition series, has provided [13] insight into factors which are important for the intercalation of such molecules into graphite. Relevant properties of the hexafluorides and the established formulations for the fully intercalated graphite salts are given in Table 23.1. The almost constant size of the hexafluorides means that for a given formulation

Table 23.1 Some properties of the third transition series hexafluorides and formulations of their graphite salts at the intercalation limit.

| | WF_6 | ReF_6 | OsF_6 | IrF_6 | PtF_6 |
|---|------------------|------------------|------------------------------|------------------------------|------------------------------------|
| dt_{2g}^n | $n = 0$ | 1 | 2 | 3 | 4 |
| Molecular volume (\AA^3) orthorhombic phase [25] | 108.5 | 106.5 | 105.7 | 105.4 | 104.6 |
| E (eV) | 3.5[26] | 5 [†] | 6.5 [‡] | 8 [‡] | 9.2 [‡] |
| Graphite Salt formulation § | no intercalation | no intercalation | $\text{C}_8^+\text{OsF}_6^-$ | $\text{C}_8^+\text{IrF}_6^-$ | $\text{C}_{12}^2\text{PtF}_6^{2-}$ |

[†] Barberi, P. and Bartlett, N., unpublished results based on $\Delta H_f[\text{O}_2\text{PtF}_6(\text{cryst.}) \text{ from } \text{O}_2(g) \text{ and } \text{PtF}_6(g)] = -60 \text{ kcal mol}^{-1}$.

[‡] Estimated values.

§ [13], this is composition at intercalation limit.

$C_x^+MF_6^-$, as may be appreciated from consideration of Fig. 23.4, the enthalpy of formation is determined mainly by the electron affinity. Since neither WF_6 nor ReF_6 will alone oxidize and intercalate into graphite, whereas the stronger oxidizers OsF_6 and IrF_6 each do so spontaneously at room temperatures, to yield first-stage materials of limiting composition $C_8^+MF_6^-$, it appears that an electron affinity superior to that of ReF_6 but less than or equal to OsF_6 is essential for the oxidative intercalation. Since the minimum value possible for the electron affinity of ReF_6 is $107 \text{ kcal mole}^{-1}$, this sets a lower limit for the electron affinity for any hexafluoride oxidizer.

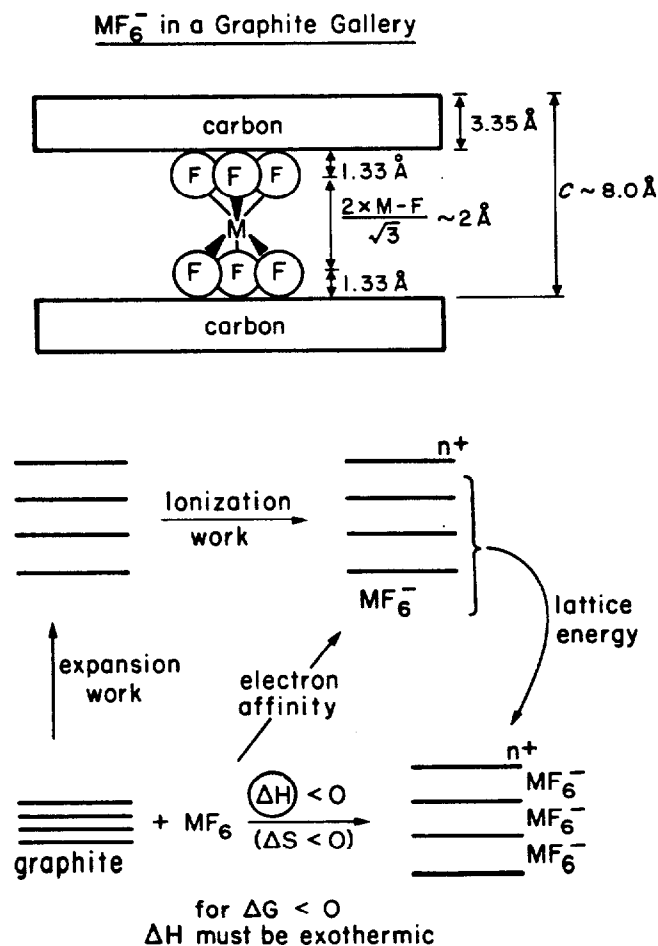


Fig. 23.4 – (a) A Born-Haber cycle for hexafluorometallate salts of graphite, $C_x MF_6^-$, and (b) MF_6^- in a graphite gallery.

Complete intercalation of single crystals of graphite by either OsF_6 or IrF_6 preserves the single crystal character for a short time [13]. A C_8MF_6 composition is characterized by a hexagonal unit cell with $a_0 = 4.92(2) \text{ \AA}$; $c_0 = 8.10(3) \text{ \AA}$; $V = 170 \text{ \AA}^3$, $Z = 1$. This represents a close packing of the guest species since, as may be seen from Table 23.1, the effective volume of a hexafluoride molecule is $>100 \text{ \AA}^3$ and the volume occupied by eight C atoms in rhombohedral graphite [14] is 70 \AA^3 . Indeed it is observed that graphite floated on liquid tungsten hexafluoride, and intercalated by OsF_6 or IrF_6 , sinks as the intercalation process comes to an end. Rough structural studies from X-ray diffraction data [11] indicate that the MF_6^- ions are, for the most part, oriented with a threefold axis parallel to the c_0 axis of the graphite as represented in Fig. 23.4. The disposition of the MF_6^- species with respect to the C atoms of the graphite grid is not established, but the model in Fig. 23.5(a) is compatible with the data for the crystal-line material.

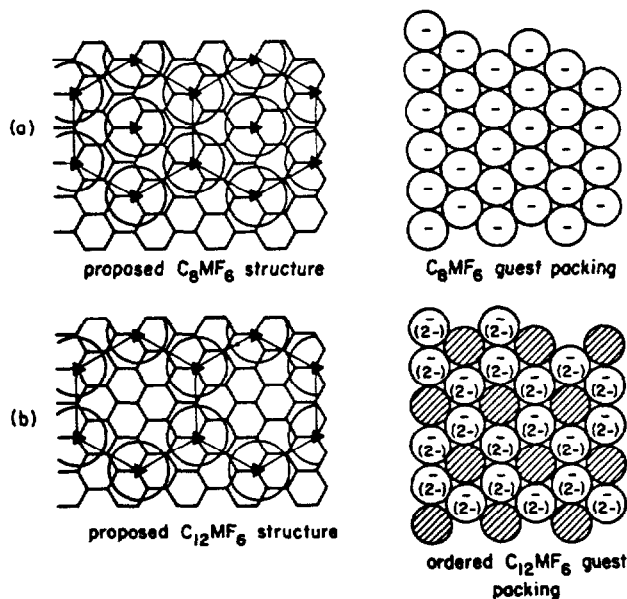


Fig. 23.5 – Models for the ordered packing of the guest species in (a) C_8MF_6 and (b) C_{12}MF_6 .

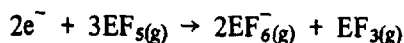
The graphite salt of composition C_8AsF_6 can be prepared by oxidizing graphite with excess $\text{O}_2^+\text{AsF}_6^-$ (or more conveniently excess $\text{C}_6\text{F}_6\text{AsF}_6$), using SO_2ClF as the solvent. The oxidation of single crystals yields, initially, material which is isomorphous with C_8OsF_6 and C_8IrF_6 . All three of these materials lose all ab plane order when kept at room temperature for several days. There appears to be no change in composition. This loss of crystallinity seems to correlate with

a marked decrease in *ab* plane electrical conductivity, observed [13] in first stage materials prepared from large pieces (5 × 5 mm × 0.5 mm) of highly oriented pyrolytic graphite (HOPG). This loss of crystallinity and decrease in conductivity could signify transfer of fluorine from MF_6^- to the carbon, but there is also the possibility that the high positive charge on the carbon layers and cooperative localization of that charge, by anions on each side of the layer (a situation peculiar to first-stage materials) may induce a distortion in the graphite layer.

The second and higher stage graphite MF_6 compounds are better behaved. The staging formula for these systems is $\text{C}_{12n}\text{MF}_6$, where *n* is the stage. Indeed only in the first stage does the gallery become filled with close-packed guests as shown in Fig. 23.5(a). The first stage is unique in having a compositional range: C_{12}MF_6 to C_8MF_6 . Obviously if we have an ordered distribution of guests in the galleries of first-stage C_{12}MF_6 , or its higher stage relatives $\text{C}_{12n}\text{MF}_6$, that arrangement will be as shown in Fig. 23.5(b). Note that the close-packed arrangement for C_8MF_6 places each ion in close contact with six similar ions, whereas the $\text{C}_{12n}\text{MF}_6$ gallery packing results in each ion having only three such neighbours. Clearly, the C_{12}MF_6 gallery packing will be energetically preferable as long as there are galleries available for occupancy. The MF_6^- salts, of second stage or higher, all appear to be good electrical conductors with specific conductivities (*ab* plane) approximately an order of magnitude better than the pristine graphite for *n* = 2. On the other hand the second stage PtF_6^{2-} salt, $\text{C}_{24}^{2+}\text{PtF}_6^{2-}$ is a relatively poor conductor, barely distinguishable from graphite itself. Again this poor conductivity may be a consequence of carbon-layer structural changes induced by the highly charged guest species.

THE INTERACTION OF ARSENIC PENTAFLUORIDE WITH GRAPHITE

The report by Vogel and his coworkers [15] of *ab* plane conductivities comparable with copper in the graphite/ AsF_5 intercalation compounds (first described by Selfig and his co-workers [16]) attracted much attention. These materials were all the more interesting to Bartlett and his coworkers for two reasons: (a) because of their possible relationship to the $\text{C}_x^+\text{AsF}_6^-$ salts and (b) because PF_5 , although physically similar to AsF_5 , was unable, alone, to form graphite intercalation compounds. It seemed to Bartlett that this difference in behaviour of AsF_5 and PF_5 was attributable to the superior electron oxidizing capability of the former. This relative capability can be expressed in terms of the enthalpies for the generalised reaction (the data for which are set out in Table 23.2):



Since the EF_6^- are biggest it is they which determine the carbon layer separation and lattice energy (see Fig. 23.4) hence such an oxidation ought to be comparable with the oxidative intercalation of graphite by the transition metal hexafluorides. It is therefore satisfying to note that the estimated enthalpy per oxidizing equivalent of AsF_5 is more exothermic than the enthalpy for the

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one-electron reduction of ReF_6 . On the other hand PF_5 is seen to be a poorer electron oxidizer than WF_6 . Significantly however PF_5 intercalated in the presence of fluorine [17] to yield a salt of limiting composition $\text{C}_8^+\text{PF}_6^-$.

Table 23.2 Enthalpy changes for electron-oxidation by gaseous AsF_5 or PF_5
(all values in kcal mole^{-1})

| | P | As |
|---|--------------------|-----------------|
| $\text{MF}_3(\text{g}) + \text{F}_2 + \text{e}^- \rightarrow \text{MF}_6^-(\text{g})$ | $\leq -158[28,28]$ | $\leq -170[27]$ |
| $2\text{MF}_3(\text{g}) + \text{F}_2 + 2\text{e}^- \rightarrow 2\text{MF}_6^-(\text{g})$ | ≤ -316 | ≤ -340 |
| $\text{MF}_3(\text{g}) \rightarrow \text{MF}_3(\text{g}) + \text{F}_2(\text{g})$ | 152[29] | 98[30] |
| $3\text{MF}_3(\text{g}) + 2\text{e}^- \rightarrow 2\text{MF}_6^-(\text{g}) + \text{MF}_3(\text{g})$ | ≤ -164 | ≤ -242 |
| Electron affinity $(3/2\text{MF}_3(\text{g}) + \text{e}^- \rightarrow \text{MF}_6^-(\text{g}) + \text{MF}_3(\text{g}))$ | ≤ 82 | ≤ 121 |

Indeed the evidence for the conversion to AsF_6^- and AsF_3 on intercalation of AsF_5 into graphite is now overwhelming. The first clear support [10] for the conversion came from arsenic-absorption-edge synchrotron-radiation spectra illustrated in Fig. 23.6. These spectra represent a true bulk property of each

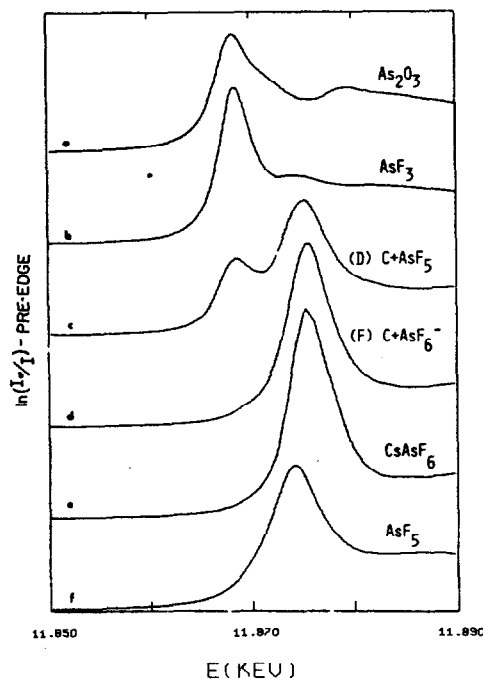
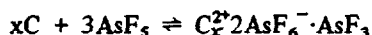


Fig. 23.6 – X-ray absorption near the As-atom absorption edge involving $1s \rightarrow 4p$ type transitions for a variety of arsenic compounds.

substance. The absorption feature which is illustrated arises from excitation of an arsenic atom 1s (core) electron to a molecular orbital of predominantly 4p character, and as seen, there is an appreciable chemical shift from one arsenic species to another. Evidently the graphite/AsF₅ material contains AsF₆⁻ and AsF₃. Such synchrotron radiation surveys have been carried out on three separate occasions on fresh samples and the findings have always been qualitatively the same. Yet there has been much reluctance to accept this simple interpretation [19]. The reason for the disagreement appears to lie in the failure of others to recognise the dynamical nature of the processes involved in the intercalation of graphite by AsF₅.

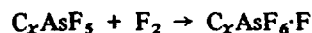
If graphite is intercalated by an appropriate molar quantity of AsF₅, in a container with small dead space (so as to generate the limiting composition material C₈AsF₅) the arsenic absorption edge spectrum clearly shows [20] the 1s → 4p type transitions characteristic of AsF₃ and AsF₆⁻. When a vacuum is applied to this material, some AsF₅ is removed at least initially, but the bulk of the volatiles proves to be AsF₃ [18]. The residual material has a composition close to C₁₄AsF₆ and the absorption-edge spectrum then indicates that the only As-containing species is AsF₆⁻. Moreover an excellent strategy for the preparation of an almost pure first stage material of composition C₁₂AsF₆ is to expose graphite to several cycles (five is adequate) of arsenic pentafluoride gas, followed by a dynamic vacuum, to constant weight. Clearly one has a dynamic equilibrium, which lies largely to the right:



The molecular species AsF₅ and AsF₃ are each removed under vacuum, but as the average charge per carbon atom decreases the concentration of AsF₅ becomes smaller.

The conversion of AsF₅ to AsF₆⁻ also accounts for the difference in the staging formulae for C_xAsF₅ and C_xAsF₆. Except for the first stage AsF₆⁻ salt, which has a compositional range C₈AsF₆ to C₁₂AsF₆, the staging formula is C_{12n}AsF₆ (n being the stage). For graphite/AsF₅ the formula [21] is C_{8n}AsF₅. If the AsF₅ is entirely converted to AsF₆⁻ and AsF₃, then each stage could be represented by the formula C_{12n}AsF₆·½AsF₃. One can view the ideal arrangement of the guest species as an anion assembly conforming to that of Fig. 23.5(b), the neutral AsF₃ molecules then residing in the vacant sites (those occupied by AsF₆⁻ in C₈AsF₆). Such an arrangement provides each charged species with only three nearest neighbours and hence a favourable Coulomb energy. A series of electrical conductance measurements and composition/stage studies [22] carried out on HOPG slabs, has established that, for second and higher stages, there is no significant difference in the conductivity of C_{12n}AsF₆·½AsF₃ (that is, C_{8n}AsF₅) and C_{12n}AsF₆. Addition of AsF₃ to C_{12n}AsF₆, to yield C_{8n}AsF₅, neither changes the stage nor the conductivity. The reverse also holds true.

The fluorination of the $C_{8n}AsF_5$ materials, as a route to $C_{12n}AsF_6$ salts, led to a surprising discovery. For second and higher stage materials the fluorine consumption was consistently that required by the equation:



The half mole of fluorine, over and above that required to form AsF_6^- , is not removed in a dynamic vacuum and the magnetic properties of $C_xAsF_6 \cdot F$ are not significantly different from those of C_xAsF_6 . Thus odd species such as F_2^- can be discounted. The extra fluorine can however be titrated by arsenic trifluoride [20,22]. Thus a $C_{12n}AsF_6$ salt can be prepared by the route:



but treatment with excess AsF_3 leads to the generation of a material indistinguishable from that prepared from graphite and AsF_5 :



The appropriate formulation for the fluorine rich materials is $C_{12n}^{2+}AsF_6^- \cdot F^-$. This requires that each of the vacant sites of the $C_{12n}AsF_6$ guest array, must contain $2F^-$, each at the poles of a hole in the AsF_6^- array (which hole is large enough to accommodate AsF_6^- itself). The puzzle is that fluorine should enter the occupied galleries of $C_{12n}AsF_6$ and not the unoccupied ones. This problem is of course related to the long standing one associated with the failure of fluorine gas to intercalate graphite [23].

It seems that the non-entry of fluorine into unoccupied galleries may simply be associated with the inability of the small F^- ion to move forward into the gallery. This ion is comparable in diameter (~ 2.7 Å) to the dimensions of a carbon-atom hexagon of the graphite layers (2.84 Å across the hexagon). Thus F^- located above such a hexagon of carbon atoms will concentrate positive charge at those atoms and will, as a consequence, lie in a deep potential well. On the other hand a F^- ion entering an occupied gallery can be imagined as forming (fleetingly) a relatively 'jelly-fish' like species such as AsF_7^{2-} , which can shed an F^- ion on a side opposite to that of F^- entry. Thus ready migration of F^- into the body of the occupied gallery could readily occur.

Clearly materials such as $C_{8n}AsF_5$, $C_{12n}AsF_6$ and $C_{12n}AsF_6 \cdot F$ provide the possibility for electrochemical interconversion and preliminary experiments indicate that such experiments are highly reversible [24]. A major point of interest is the high oxidizing potential of $C_{24}AsF_6 \cdot F$, which, although not a good conductor, is no worse than graphite. Such materials should be excellent for electrochemical fluorination. They themselves have marked resistance to oxidation. Because the carbon layers maintain the form of the material and serve as the source and sink

for electrons, such materials can in principle be cycled indefinitely through redox cycles and are therefore of prime interest as a basis for energy storage systems.

CONCLUSION

Although powerful oxidizers such as transition metal hexfluorides, O_2^+ salts, and Lewis fluoroacids in combination with fluorine can be successfully applied to the electron oxidation of a wide variety of electron delocalized systems, it is in the oxidation of the mundane polymeric material graphite where the most surprising, intellectually satisfying, and potentially most important findings have been made. But there is a sense of just being at the beginning of an important enterprise.

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